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A Determination of V_2O_5 Activity in Corrosive Molten Vanadate-Sulfate Phases

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ABSTRACT

Although aggressive hot corrosion by molten vanadate-sulfate deposits in boilers and engines burning low-quality fuel has been known for 75 years or more, there is surprisingly little data in the literature on the thermochemistry of vanadate-sulfate melts, especially as to the activity of the corrosive V_2O_5 component. We have recently devised a thermogravimetric (TGA)/ SO_3 equilibrium technique that could potentially be used to "chart" the V_2O_5 activity in vanadate-sulfate melts over a wide range of Na/V ratios, SO_3 partial pressures and temperatures. The method is illustrated in a study of the reaction of CeO_2 with a $NaVO_3$ - Na_2SO_4 - V_2O_5 - SO_3 melt system ($Na/V = 1$) at $800^\circ C$. Results from the study define the conditions under which CeO_2 will be chemically nonreactive with the melt, and also show the V_2O_5 activity coefficient to be, for the given experimental conditions, of the order of 1×10^{-2} .

INTRODUCTION

Hot corrosion by molten vanadate-sulfate deposits resulting from vanadium and sulfur fuel impurities has been a recognized problem in boilers and engines for many years. One may wonder, however, why study vanadate-sulfate hot corrosion when the U.S. military, along with the civilian sector, is presently being pushed to burn only clean fuels because of environmental concerns. The primary answer, of course, is that in war there can be no guarantee of always

having clean fuel for our ship, tank and truck engines. It is important therefore that, even though "clean fuel" use is planned, we have engine materials and coatings that can tolerate low quality fuel if the wartime need arises.

A knowledge of the chemistry of vanadate-sulfate hot corrosion also has "dual usage" since many hot corrosion reactions are related to the reactions that can be used to clean up fuel. The removal of SO_3 from smoke stack gases by CaO or MgO additives, for example, involves the same type of chemical reactions as molten sulfate-induced hot corrosion. Similarly, the reaction between yttria (Y_2O_3) and V_2O_5 to form highly stable YVO_4 , which causes degradation of Y_2O_3 -stabilized zirconia thermal barrier coatings in engines burning vanadium-contaminated fuel, has been recently "turned around" and used as the basis for a yttrium-based fuel additive for the prevention of hot corrosion by vanadium-containing fuels (1).

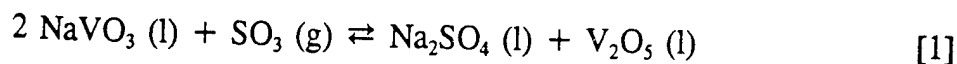
Attempts in the past to apply thermodynamics to predict and/or prevent hot corrosion have had limited success, perhaps partly because the difference in fuel impurity levels between "corrosive" and "noncorrosive" fuels is often small. Hot corrosion does not simply increase monotonically with fuel level, but frequently shows strongly accelerated attack for only small increases in fuel contaminants. For example, little hot corrosion is seen with aviation-quality ($< 0.05\% \text{ S}$) gas turbine fuel, whereas extensive hot corrosion has been encountered with marine-quality fuel ($< 1\% \text{ S}$), although the actual difference in sulfur content may be only 10-20X. In "low temperature" hot corrosion, even very small changes in the combustion gas SO_3 partial pressure can determine whether engine deposits of eutectic $\text{CoSO}_4\text{-Na}_2\text{SO}_4$ will be molten or not (2), which in turn can drastically effect the severity of hot corrosion (3,4). Vanadate hot corrosion has a similar short range of criticality, with vanadate-accelerated corrosion being generally negligible for V levels in fuel below 0.1 ppm, but often aggressive at V concentrations of only 1-10 ppm.

The importance of such small, but critical, changes in the fuel contaminant level is difficult to distinguish in the thermodynamic treatment of molten salt systems, since their energy effect is often hardly more than the probable error associated with much of our available thermodynamic data. For example, as shown below, a 10X change in the V_2O_5 concentration (or equivalently, the V_2O_5 activity coefficient) in a simulated vanadate-sulfate engine deposit typically corresponds to a difference of only about -10 kJ amidst calculations involving Gibbs energies of -1000 to -1500 kJ/mol, where each Gibbs energy may have a probable error of ± 2 kJ/mol or more. There is a strong need therefore for more accurate thermodynamic data, especially standard Gibbs energies of formation and activity

coefficients in melts, if thermodynamics are to be used with maximum effectiveness in predicting and/or preventing vanadate-sulfate hot corrosion.

The problem is compounded also by the uncertainty that still exists as to which "solution model" should be used for melts involving strong acid-base species such as Na_2O , K_2O , SO_3 , SiO_2 , V_2O_5 , etc. The solution model represents the framework by which the thermodynamicist seeks to describe how the activities of the various melt components change with concentration. In some cases, no solution model has been invoked, and the melts are simply assumed to be ideal (i.e., where the activity coefficient, γ , is unity, and the activity is equal to the mole fraction of the species). For example, Hwang and Rapp (5) assume that the Na-V-S-O systems at 900°C give ideal solution behavior, and that the activities of the component species can be equated to their molar concentrations. On the other hand, Bonnell and Hastie (6) believe that strong acid-base systems can be highly nonideal, with the activity of such species as Na_2O changing by many orders of magnitude over a narrow concentration range in some cases. Bonnell and Hastie have developed a solution model, the Ideal Mixing of Complex Components (IMCC) model, which they advocate as giving the best description of the solution behavior in strong acid-base melts. Numerous other possible solution models for melts have been proposed, however, as discussed, e.g., in the Proceedings of the Sixth International Conference on High Temperatures--Chemistry of Inorganic Materials (7).

In our own experience, we have found nonideal behavior for reaction [1],



which is, according to the thermodynamic calculations of Luthra and Spacil (8), the probable predominant reaction in blade deposits in gas turbine engines burning V- and S-containing fuels under normal marine operating conditions. Using a thermogravimetric analysis (TGA)/ SO_3 equilibrium technique (9), we equilibrated NaVO_3 at 700°C and 800°C with fixed partial pressures of SO_3 ranging from 1×10^{-7} to 1×10^{-3} atm, and determined the equilibrium weight gain resulting from the uptake of SO_3 . From this data, we were able to calculate the mole fraction of V_2O_5 experimentally formed by reaction [1], which we then subsequently compared with the "ideal behavior" expected for reaction [1], as explained below.

The activity, a_i , of a given species is described by

$$a_i = \gamma_i \cdot X_i \quad [2]$$

where γ_i is the activity coefficient, and X_i is the mole fraction. If the species gives ideal solution behavior, then the activity coefficient is equal to 1, and the activity is simply the mole fraction of the species.

For reaction [1], we have

$$\Delta G_T^\circ = -RT \ln K \quad [3]$$

where R is 8.3144 joules/degree-mole and T is 1073° K (i.e., for 800° C conditions), while

$$K = (a_{V_2O_5})(a_{Na_2SO_4})/(a_{NaVO_3})^2(P_{SO_3}) \quad [4]$$

and ΔG_T° is determined by

$$\Delta G_T^\circ = \sum \Delta_f G_{T, \text{Products}}^\circ - \sum \Delta_f G_{T, \text{Reagents}}^\circ \quad [5]$$

If reaction [1] follows ideal solution behavior, then using the standard Gibbs energies of formation for $NaVO_3$ (l), SO_3 (g), Na_2SO_4 (l) and V_2O_5 (l) provided by Luthra and Spacil (8), we can reduce equation [3] to

$$K \cdot P_{SO_3} = (MF_{V_2O_5})(MF_{Na_2SO_4})/(MF_{NaVO_3})^2 \quad [6a]$$

or, as a quadratic equation,

$$91.61166 \cdot P_{SO_3} = x^2/(1-2x)^2 \quad [6b]$$

Solving equation [6b] by numerical approximation on the computer then yields the ideal mole fraction of V_2O_5 that should be formed at each given SO_3 partial pressure.

The experimental mole fraction of V_2O_5 was determined by converting the weight of SO_3 taken up in reaction [1] to reflect the millimoles of Na_2SO_4 and V_2O_5 formed, as well as the millimoles of $NaVO_3$ consumed, and calculating the resultant mole fraction of V_2O_5 . (Note that the amount of free SO_3 contained in the melt is so small that it can be ignored in this calculation.) The ideal vs. experimental mole fractions of V_2O_5 formed at the different SO_3 partial pressures are compared in Table 1, which also shows that division of the ideal V_2O_5 mole

TABLE 1

Experimental vs. Ideal Solution Mole Fractions of V_2O_5
Formed at 800°C at the SO_3 Partial Pressures Indicated

P_{SO_3} (atm)	Wgt. Gain (mg/50mg NaVO_3)	Ideal $M-F_{V_2O_5}$	Exptl. $M-F_{V_2O_5}$	"Activity Coeff.", γ
1×10^{-7}	2.0	0.003	0.06	0.05
1×10^{-6}	2.8	0.009	0.08	0.11
1×10^{-5}	4.0	0.028	0.12	0.23
1×10^{-4}	8.0	0.078	0.24	0.33
1×10^{-3}	11.0	0.18	0.34	0.53

fraction by the experimental V_2O_5 mole fraction yields an "activity coefficient" that indicates the nonideality of the V_2O_5 solution behavior. This "activity coefficient" is not quantitative, however, because the actual V_2O_5 activity in the melt is not (since $a_{V_2O_5} \neq a_{\text{Na}_2\text{SO}_4}$) the ideal V_2O_5 activity calculated here.

In the present paper, we describe a means, derived in a study of the reaction of CeO_2 with the NaVO_3 - SO_3 system at 800°C (10), by which it in fact appears possible to obtain quantitative values for the V_2O_5 activity coefficient in vanadate-sulfate melts.

EXPERIMENTAL

Our experiments were conducted using a Cahn 1000 thermobalance (Fig. 1) fitted with a system for controlling, and analyzing, the SO_2 concentration in the furnace input air stream. The SO_3 concentration was then established by equilibrating the SO_2 -air mixture over a Pt catalyst at

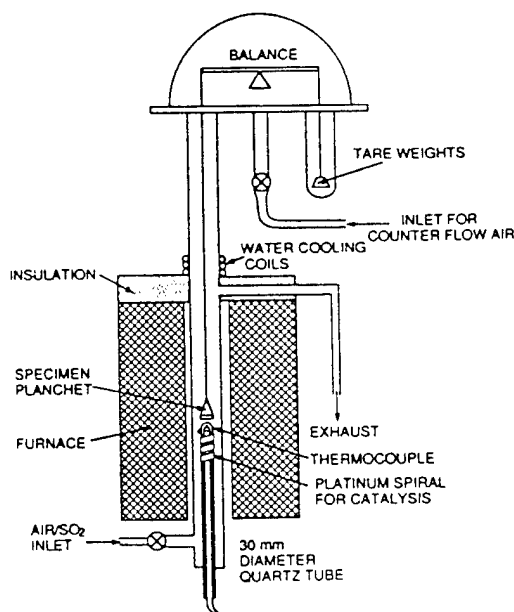


Fig. 1 Thermobalance/Furnace System

temperature in the furnace. Details of the experimental apparatus and procedure were published previously (9).

In the investigation, we first established a "baseline" curve of equilibrium weight gain vs. SO_3 partial pressure at 800°C for 50 mg (0.41 mmols) of pure NaVO_3 . We then ran duplicate experiments using just the same conditions except that 17 mg (0.1 mmols) of CeO_2 was now mixed with the 50 mg of NaVO_3 . The weight gain curve (Fig. 2) for $\text{CeO}_2\text{-NaVO}_3$ was just the same as for NaVO_3 alone (100% NaVO_3) up to the SO_3 partial pressure at which the V_2O_5 activity of the melt was increased sufficiently, by reaction [1], that reaction [7] could commence:



X-ray diffraction was used to confirm that only CeO_2 exists in the melts at SO_3 partial pressures below the critical P_{SO_3} for reaction [7], and that CeVO_4 is formed above this SO_3 partial pressure.

RESULTS AND DISCUSSION

Our experimental data are summarized in Fig. 2. The weight gain for $\text{CeO}_2\text{-NaVO}_3$ as a function of SO_3 partial pressure is the same as for NaVO_3 alone up to an SO_3 pressure of $2\text{-}3 \times 10^{-6}$ atm. The absence of any extra increment of weight gain at the lower SO_3 partial pressures shows that CeO_2 is chemically inert (just as the Pt weighing planchet is) to the $\text{NaVO}_3\text{-SO}_3$ system over this lower P_{SO_3} range.

However, an additional increment of weight gain begins to occur at $2\text{-}3 \times 10^{-6}$ atm of SO_3 , which marks the onset of reaction [7] where $\text{CeO}_2 \rightarrow \text{CeVO}_4$. The extra weight gain arises by the following mechanism. The Na_2O , V_2O_5 and SO_3 components of the melt are interrelated through two dissociation reactions,

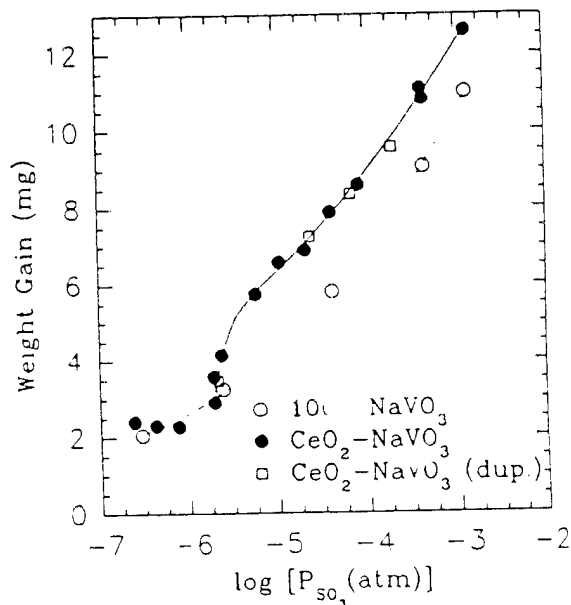
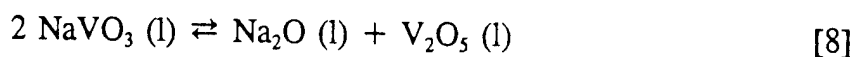
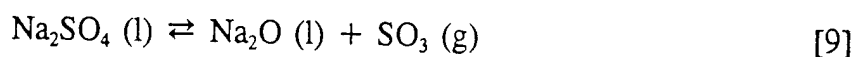


Fig. 2 Wgt. gain vs P_{SO_3} for NaVO_3 and $\text{CeO}_2\text{-NaVO}_3$ at 800°C .

one involving NaVO_3 ,



and the other, Na_2SO_4 ,



(Note that reversing reaction [9], and then adding reactions [8] and [9] to "cancel out" $\text{Na}_2\text{O} (\text{l})$ yields reaction [1].) When V_2O_5 begins to be consumed from the melt via reaction [7], this increases the Na_2O activity in the melt through reaction [8]. The increased Na_2O activity, in turn, allows more SO_3 to enter the melt to form additional Na_2SO_4 by reaction [9]. The combined reactions thus result in a "weight gain step" just at the P_{SO_3} at which reaction [7] commences.

The theoretical weight gain, by way of reactions [7]-[9], for the conversion of 0.1 mmols of CeO_2 totally to CeVO_4 is 3.2 mg. In an ideal, infinite system, one would thus expect a "vertical step" additional weight gain increment of 3.2 mg just at the critical P_{SO_3} at which reaction [7] becomes possible. In contrast, the maximum observed weight gain increment in Fig. 2 is only slightly more than 2 mg. However, subsequent work (10) since these initial experiments has confirmed that the experimental weight gain does in fact approach the theoretical value when higher dilutions (i.e., more NaVO_3 to CeO_2) are used. The failure to obtain full theoretical weight in Fig. 2 for $\text{CeO}_2 \rightarrow \text{CeVO}_4$ is therefore probably only the result of the experimental conditions.

In earlier work (11), we determined the solubility of CeO_2 in molten NaVO_3 at 800°C to be approximately 0.2 mole percent, and showed also that CeVO_4 crystals were precipitated at temperature from molten deposits produced by equilibrating NaVO_3 on ceria-stabilized zirconia at 700°C with SO_3 . In the latter case, the residual molten deposits were so depleted of vanadium (being strongly converted to sulfates) that no V could be detected by energy dispersive x-ray analysis. Only minimal solubility of the initial CeO_2 in 800°C NaVO_3 (less than 1/125 of the total CeO_2 present), or of the CeVO_4 product in the reaction melt, is expected therefore in the present experiments.

If ideal behavior is assumed, then the Gibbs energy for reaction [7], and an "ideal" Gibbs energy of formation for CeVO_4 , can be calculated as follows. As shown in Fig. 2, the amount of weight gain of the melt before reaction [7] begins is 3.0 ± 0.2 mg. This weight gain represents the uptake of 0.0375 mmols of SO_3 which, by reaction [1], corresponds to the formation of 0.0375 mmols

each of Na_2SO_4 and V_2O_5 , and the consumption of 0.075 mmols of the 0.41 mmols of NaVO_3 originally present. The resultant mole fraction of V_2O_5 is 0.091 which, for ideal behavior, equates to a V_2O_5 activity in the melt of 0.091. This is the V_2O_5 activity at which reaction [7] just begins, and for reaction [7] we therefore have the thermodynamic relationship,

$$\Delta G^\circ_{1073\text{K}} = -RT \ln \frac{(a_{\text{CeVO}_4})^2 (P_{\text{O}_2})^{0.5}}{(a_{\text{CeO}_2})^2 (a_{\text{V}_2\text{O}_5})} \quad [10]$$

where, as pure solids, CeVO_4 and CeO_2 have activities of 1, and the activities of O_2 in the air and V_2O_5 are 0.21 and 0.091, respectively. This yields a calculated $\Delta G^\circ_{1073\text{K}}$ for reaction [7] of -14.422 kJ, where the experimental uncertainty is ± 0.4 kJ assuming the melt weight gain to be 3.0 ± 0.2 mg, the weight of the initial NaVO_3 to be 50.0 ± 0.5 mg, and the temperature to be $1073 \pm 5^\circ \text{K}$. Taking the Gibbs energies of formation for CeO_2 (s) and V_2O_5 (l) at 800°C as -865.890 kJ/mol and -1098.211 kJ/mol (12), we can then derive, as indicated by equation [5], an "ideal" standard Gibbs energy of formation of CeVO_4 (s) at 800°C of -1422.207 kJ/mol.

There are no experimental $\Delta_f G^\circ$'s for CeVO_4 in the literature to compare with this "ideal" value, but Yokokawa *et al* (12) have estimated the Gibbs energy of formation of CeVO_4 (s) at 800°C as -1444.785 kJ/mol. This gives agreement to within about 20 kJ/mol. However, we know from our earlier study (9) that the NaVO_3 - V_2O_5 - Na_2SO_4 melt system is clearly nonideal, with the V_2O_5 activity coefficients being of the order of 0.1 to 0.01 at the lower V_2O_5 concentrations (Table 1). If V_2O_5 activity coefficients of 0.1, 0.01, etc. are introduced into equation [10], the resultant $\Delta_f G^\circ_{\text{CeVO}_4}$ becomes about 10 kJ/mol more negative for each 10X reduction in the activity coefficient, and equals -1442.749 kJ/mol for a V_2O_5 activity coefficient of 0.01. This last value agrees very well with the $\Delta_f G^\circ_{\text{CeVO}_4}$ of -1444.785 kJ/mol estimated by Yokokawa *et al*, and we take the agreement therefore as indicating that a $\Delta_f G^\circ$ for CeVO_4 at 800°C of about -1445 kJ/mol, and a V_2O_5 (l) activity coefficient in the melt of about 0.01, are both essentially correct.

Our TGA/ SO_3 equilibrium technique can be expanded to include different temperatures, vanadate-sulfate melt compositions (i.e., by using different Na/V ratios in the initial vanadate deposit), and "indicator" reaction pairs (i.e., $\text{CeO}_2 \rightarrow \text{CeVO}_4$). We have shown earlier (9), for example, that $\text{Sc}_2\text{O}_3 \rightarrow \text{ScVO}_4$ at $\sim 5 \times 10^{-6}$ atm of SO_3 , and $\text{In}_2\text{O}_3 \rightarrow \text{InVO}_4$ at $\sim 5 \times 10^{-4}$ atm of SO_3 , in the NaVO_3 - SO_3 system by reactions analogous to $\text{CeO}_2 \rightarrow \text{CeVO}_4$. The TGA/ SO_3 equilibrium

technique therefore has the potential to provide, by a series of studies of the various oxide \rightarrow vanadate reactions over an array of different sulfate-vanadate melt compositions and temperatures, the high accuracy thermodynamic data (including Gibbs energies of formation, activity coefficients, solution models, etc.) that are needed to understand and predict the reaction behavior of high temperature oxides with vanadate-sulfate melts.

CONCLUSIONS

A thermogravimetric analysis (TGA)/SO₃ equilibrium study of the reaction of CeO₂ with the NaVO₃-SO₃ system at 800° C shows CeO₂ to be inert to chemical reaction with the NaVO₃-SO₃ melt at SO₃ partial pressures up to $2-3 \times 10^{-6}$ atm, with CeVO₄ being formed above this SO₃ partial pressure.

Thermodynamic analysis of the reaction data indicates the $\Delta_f G^\circ$ for CeVO₄ (s) at 800° C as being -1445 kJ/mol, and the V₂O₅ activity coefficient of the melt at the point of CeVO₄ formation as being approximately 1×10^{-2} .

The TGA/SO₃ equilibrium technique has the potential to significantly increase our knowledge of the thermochemistry and melt solution chemistry involved in the reactions of high temperature oxides with molten vanadate-sulfate melts.

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